A Rigorous Derivation of the Entropy Bound and the Nature of Entropy Variation for Non-equilibrium Systems during Cooling

P. D. Gujrati*

Department of Physics, Department of Polymer Science,

The University of Akron, Akron, OH 44325

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Abstract

We use rigorous non-equilibrium thermodynamic arguments to prove (i) the residual entropy of any system is bounded below by the experimentally (calorimetrically) determined absolute temperature entropy, which itself is bounded below by the entropy of the corresponding equilibrium (metastable supercooled liquid) state, and (ii) the instantaneous entropy cannot drop below that of the equilibrium state. The theorems follow from the second law and the existence of internal equilibrium and refer to the thermodynamic entropy. They go beyond the calorimetric observations by Johari and Khouri [J. Chem. Phys. **134**, 034515 (2011)] and others by extending them to all non-equilibrium systems regardless of how far they are from their equilibrium states. We also discuss the statistical interpretation of the thermodynamic entropy and show that the conventional Gibbs or Boltzmann interpretation gives the correct thermodynamic entropy even for a single sample regardless of the duration of measurements.

I. INTRODUCTION

In a recent publication, Johari and Khouri[1] used upper and lower bounds on the isobaric entropy $S(T_0)$ of a glass as a function of the temperature T_0 of the surrounding medium, obtained by using the measured heat capacity during cooling and heating to argue for the reality of the residual entropy S_{R}, as the latter has become a highly debated issue in the literature.[2–11] For a brief review of the history of the residual entropy and the current controversy, we refer the reader to Goldstein,[9] Gutzow and Schmelzer,[12] Nemilov,[13] and the recent reviews[14,15] by us; see also below. The existence of a non-zero residual entropy $(S_{\mathrm{R}} > 0)$ is very common in Nature, and does not violate Nernst's postulate, as the latter is applicable only to equilibrium states with a *non-degenerate* ground state; see Sect. 64 in Landau and Lifshitz.[16] Its existence was first theoretically demonstrated by Pauling and Tolman;[17] see also Tolman.[18] In addition, the existence of the residual entropy has been demonstrated rigorously for a very general spin model by Chow and Wu.[19] The residual entropy for glycerol was observed by Gibson and Giauque[20] and for ice by Giauque and Ashley.[21] Pauling[22] provided the first numerical estimate for the residual entropy for ice, which was later improved by Nagle.[23] Nagle's numerical estimate has been recently verified by simulation.[24,25] The numerical simulation carried out by Bowles and Speedy[26] for glassy dimers also supports the existence of a residual entropy. Richet[27] uses the Adam-Gibbs theory to justify the residual entropy. Thus, it appears that the support in favor of the residual entropy is quite strong. We wish to emphasize that what is customarily called the third law due to Nernst, according to which the entropy must vanish at absolute zero, is merely a postulate and not a strict theorem even in equilibrium.[16,28,29] Indeed, many exactly solved statistical mechanical models show a non-zero entropy at absolute zero. However, as of yet, no experiment can be performed at absolute zero to demonstrate the residual entropy; in all cases, some sort of *extrapolation* is required. This point should not be forgotten in the following whenever we speak of measuring the residual entropy. In addition, we will speak of the equilibrium state associated with a non-equilibrium state. Depending on the context, the equilibrium state may represent a true equilibrium state such as a crystal or a (time-independent) metastable state such as the supercooled liquid. However, for the purpose of clarity, we will consider the supercooled liquid in the following, but the arguments are applicable to both cases.

A. Controversy and Its Current Status

It is surprising to see this controversy persist in the current literature even though it seemed resolved a long time ago;[17,18] we also note somewhat recent attempts.[30,31] The controversial issue is the following: As the irreversibility does not allow for an exact evaluation of the entropy, is it possible for the entropy to decrease by an amount almost equal to S_R within the glass transition region so that the glass (see Glass2 in Fig. 1) would have a vanishing entropy at absolute zero? The entropy for Glass2 follows from the recent proposals by Kivelson and Reiss,[7] and by Gupta and Mauro;[8,10,32] see also Reiss.[33] Gupta and Mauro[32] conclude that

$$S \leq S_{\mathrm{SCL}} \tag{1}$$

at and below the glass transition, in conformity with Glass2. They actually state the above inequality at the glass transition in Eq. (10) of the above paper but then take it to be also valid below the transition. Their conclusion is based on the fact that $G \geq G_{\mathrm{SCL}}$ for the Gibbs free energies and the equality $H = H_{\mathrm{SCL}}$ of the enthalpy at the glass transition; here S, G and H refer to the glass and $S_{\mathrm{SCL}}, G_{\mathrm{SCL}}$ and H_{SCL} refer to the supercooled liquid. The equality $H = H_{\mathrm{SCL}}$ is widely accepted as an experimental fact in the field.[34,36] The motivation for their proposal is their understanding[7,8,10,32,33] that the entropy of a single sample of glass at absolute zero must be zero as the microstate of the sample will not change no matter how long the glass is "observed." Thus, according to this view, the entropy is not merely less than that of Glass1, such as Glass3, it must be strictly less than or equal to S_{SCL}. The alternative shown as Glass3

$$S < S_{\mathrm{Glass1}} > S_{\mathrm{SCL}} \tag{2}$$

is not consistent with this view.[32]

According to Eq. (1), the entropy of a glass can only increase during relaxation as the glass strives to equilibrate at any temperature below the glass transition. What could be wrong with such a simple deduction, which does not require any sophisticated mathematics? Gutzow and Schmelzer[12] (see the discussion following their Eq. (39)) also come to the same conclusion. On the other hand, the common view of the glass is shown by Glass1 in Fig. 1, with the clear implication that the entropy of the glass is higher than that of the supercooled liquid. There is at present no consensus as is evident from the discussion reported in the proceedings,[2] and the general conclusion drawn by Goldstein[9] that the abrupt entropy loss
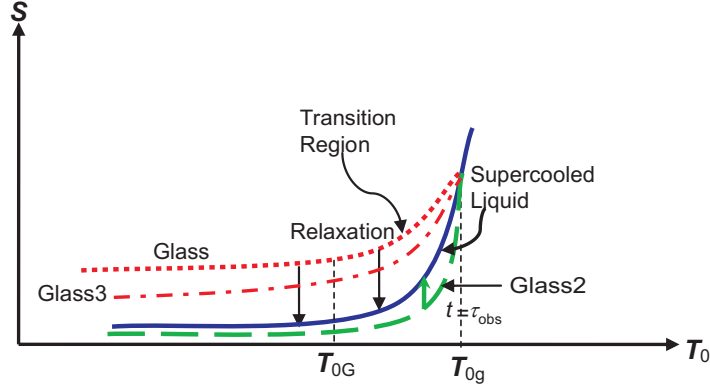
FIG. 1: Schematic behavior of the entropy: equilibrated supercooled liquid (solid curve) without any relaxation and three possible glasses (Glass1-dotted curve, Glass2-dashed curve, Glass3-dash-dotted curve) during vitrification as a function of the temperature T_0 of the medium. Structures appear to freeze (over an extremely long period of time) at and below T_{0G}; see text. The transition region between T_{0g} and T_{0G} over which the liquid turns into a glass has been exaggerated to highlight the point that the glass transition is not a sharp point. For $T_0 < T_{0g}$, the non-equilibrium state undergoes isothermal structural relaxation in time towards the supercooled liquid. For Glass1, the two vertical downward arrows show isothermal structural relaxation at two different temperatures, during which the entropy decreases. The same will also happen for Glass 3. For Glass2, the entropy increases during isothermal structural relaxation; see the upward arrow. The instantaneous temperature $T(t)$ of the glass decreases towards the T_0 during relaxation., so that the entropy is a function of $T(t)$ during relaxation. The entropy of the supercooled liquid is shown to extrapolate to zero per our assumption, but that of Glass1 to a non-zero value and of Glass2 to zero at absolute zero. The entropy of Glass 3 may or may not vanish at absolute. The possibility of an ideal glass transition, which does not affect our conclusion, will result in a singular form of the solid curve. The second law is used to support Glass1 and rule out Glass2; see the text.

comparable to S_R as proposed by Kivelson and Reiss[7,33] will result in the construction of a perpetual motion machine of the second kind. Goldstein merely follows the consequence of the existence of a possible reversible connection between a glass and the supercooled liquid as

proposed by Kivelson and Reiss. In view of the simple observation in Eq. (1), one can argue that the general demonstration by Goldstein is either inapplicable to a glass or that the basic premise of a possible existence of a reversible connection between a glass and the supercooled liquid using Kivelson-Reiss construction must be invalid. Indeed, Gupta and Mauro[8,10] argue that the second law does not apply to the glass transition proposed by them as the loss of entropy in their formulation does not result in a latent heat, while Goldstein's general demonstration noted above depends crucially on this heat and, therefore, does not invalidate the proposal of a discontinuous loss by Gupta and Mauro although it does invalidate the proposal by Kivelson and Reiss. One can also argue that the special "electrode" construction proposed by Kivelson and Reiss, and used by Goldstein, requires *microscopic* information to confine the system into a *unique* basin, a configurational microstate, in that one needs to know precisely where *each* particle of the system is located within a certain small volume cell associated with its possible vibrations;[37,38] see Gujrati[15] for elaboration on microstate measurements. Oppenheim[39] has also raised somewhat of a similar objection. In addition, it is not obvious that thermodynamics, which is a description of a macrostate, can be applicable to a microstate such as the one obtained by the above special construction.

Mauro et al[2] also consider a glass formed by continuous cooling such as Glass2 in which the entropy is lost continuously. It should be noted that Goldstein[9,40] does not explicitly discuss continuous cooling; however, in a private discussion, Goldstein has pointed out that his demonstration based on solubility also covers continuous cooling. The amount of loss in this case is not going to be close to S_{R}. Therefore, Goldstein's argument will not only invalidate Glass2 but also Glass3.

Despite all these attempts, the situation remains confusing, in part because, to quote Goldstein[40]: "As the residual entropies found by calorimetric measurements either equal or at least do not exceed the calculated value...., it is generally though not unanimously accepted that the residual entropies are real." Thus, in these cases, as already pointed out by Bestul and Chang,[41] one "...cannot demonstrate..." whether the residual entropy "...differs from zero." Of course, the attempts so far by those who believe in the residual entropy,[1,3,12,13,31] have been only to demonstrate that the residual entropy is *approximately* equal to the calculated value, to be denoted here by $S_{\mathrm{expt}}(T_0)$, within a few percentages; however, as they do not deal directly with S_{SCL}, they have not ruled out the inequality in Eq. (1). Even though no experiments have revealed a situation in which $S_{\mathrm{expt}}(T_0)$ lies below

$S_{\text{SCL}}(T_0)$ over the temperature range where the latter has been experimentally determined, the above calorimetric studies make no claim that

$$S_{\text{expt}}(T_0) > S_{\text{SCL}}(T_0) \tag{3}$$

for all temperatures below the glass transition, even though many workers believe it to be intuitively true. In light of Eq. (1), however, t is possible that the above inequality turns out to be incorrect. The contribution of Goldstein[9] only proves that an abrupt or a continuous loss of a part of the residual entropy ($S < S_{\text{Glass1}}$) cannot be valid, but it neither rules out zero residual entropy nor the inequality in Eq. (1). It also says nothing about the above inequality. Is it possible that the demonstration of $S \leq S_{\text{SCL}}$ itself is invalid? However, we cannot find any discussion of it in the current literature. Thus, it is not surprising that the controversy still persists. Goldstein[9] has suggested that the entropy loss proposal "...may be impossible to verify by any conceivable experiment,..." thus leaving the possibility that some theoretical approach, such as the one to be taken here, may resolve the issue. A theoretical approach will also allow us to investigate the inequalties in Eqs. (1-3) at absolute zero, where experiments cannot be performed.

B. Clausius Limits

Johari and Khouri[1] have analyzed data from a large number of glasses to draw the conclusion that a non-zero residual entropy is real in the cases they have analyzed. The idea behind their discussion is simple: the bounds, called the Clausius limits,[1] on the (thermodynamic) entropy reflect the contributions of irreversibility in the experimentally determined estimate $S_{\text{expt}}(T_0)$ of the entropy $S(T_0)$. They find that the two bounds are so tight in most cases (less than 2%) that one can neglect the corrections to the calorimetrically determined $S_{\text{expt}}(T_0)$ due to irreversibility along cooling and heating paths, a conclusion arrived at by several others.[1,3,12–14] It appears that this approach was first used by Bestul and Chang[41] and later by Sethna and coworkers.[31]. Johari and Khouri finally conclude that the experimental evidence of a non-zero residual entropy (see Glass1 in Fig. 1) is beyond reproach for the systems they have analyzed. The implication of their contribution and of several others mentioned above[3,12,13,31] is that there is no thermodynamic reason, such as the third law, for the residual entropy to be zero, a conclusion well known in theoretical physics.[16]

We should mention at this point that if there is ever any *conflict* between the second law[42] and any other law in physics such as the zeroth or the third law for a macroscopic body, it is the second law that is believed to hold in *all* cases. This suggests that Glass2 does not materialize for the systems considered by Johari and Khouri.[1]

C.   Importance of Bounds

We wish to prove in this work that Glass2 cannot materialize for any system. As far as Glass3 is concerned, we will establish that it may represent an approximation for Glass1, but cannot represent a real glass. Therefore, we will mostly consider Glass1 and Glass2 in the following. To fulfill this goal, we have to go beyond the calorimetric evidence[1,3,12,13] for the residual entropy. We treat the two glasses in Fig. 1 basically as two separate *proposals* for the general behavior of glasses. Therefore, they need to be demonstrated to be valid or invalid in *all* cases, without a single exception. To obtain such a general result, we must not *make* any assumptions or approximations; the latter would mean that the conclusion could not be valid in all cases; see below. We must also not rely upon heuristic or intuitive arguments as part of the proof. As the exact values of the entropy require detailed information about the system, it in not feasible to find the two entropies exactly for all systems. Thus, we will not be interested in system-specific knowledge; rather, we want mathematically sound conclusions about the entropy that will be valid for all glass formers *without exception.* Because the controversy is between two inequalities, any approximation would turn the strict inequality such as $S < S_{\mathrm{SCL}}$ into $S^{\mathrm{approx}} \lessapprox S_{\mathrm{SCL}}$. In that case, we may have $S > S_{\mathrm{SCL}}$ in some cases depending on how far S is from S^{approx}. Unfortunately, various discussions[1,3,12,13] in favor of the residual entropy and the specific critique by Goldstein[9] using solubility either use approximations (such as replacing the inequality in Eq. (9) below by an equality) or are phenomenological with a limited domain of validity. Indeed, Gutzow and Schmelzer[12] have come to the conclusion (see above Eq. (40) there) that in any real process, the entropy either remains constant or increases. The conclusion is in accordance with Eq. 1. Thus, the current status of the field leaves open the possibility that the residual entropy could vanish.

It is abundantly clear from the above discussion that there is a need to look at the issue of residual entropy once again. In our opinion, the real issue is the inequality in Eq. (1), whose validity has not been scrutinized in the literature. If the bound is jusitified, it automatically

proves that S_R is not real. If, on the other hand, the bound is not justified, it does not automatically prove that S_R is real. We then have the additional task to prove its reality. As is customary, we treat the supercooled liquid as an equilibrium state, even though it not a true equilibrium state; see above. We proceed by following the strict second law inequality $d_i S > 0$ in Eq. (8) and use it along with the existence of internal equilibrium[43] (for Theorem 2) to prove the following two theorems applicable to *all* non-equilibrium systems, regardless of how close or far they are from their equilibrium state.

Theorem 1 *The experimentally observed non-zero entropy at absolute zero in a vitrification process is a strict lower bound of the residual entropy of any system:*

$$S_R \equiv S(0) > S_{expt}(0) > S_{SCL}(0). \tag{4}$$

Theorem 2 *Any drop of the glass entropy below that of the supercooled liquid (such as Glass2 in Fig. 1) is a violation of the second law.[42] Thus,*

$$S > S_{SCL}, \tag{5}$$

so that the entropy variation in time has a unique direction as shown by the downward arrows *in Fig. 1.*

Our conclusion in Eq. (5) is in contradiction with that in Eq. (1). Therefore, we need to understand the reason for this discrepancy. All experiments on or exact/approximate computations for non-equilibrium systems *must* obey the strict inequalities in Eqs. (4-5) without any exception. This is the meaning behind the usage of "... rigorous ..." in the title of the paper. The actual values of the entropy are not relevant for the aim of this work, which is to settle the controversy between Glass1 and Glass2 under vitrification and the way their entropies relate to that of the equilibrated supercooled liquid. Because of the possibility that the systems may be far away from equilibrium, where the irreversible contributions may not be neglected, our results go beyond the previous calorimetric evidence.[1,3,12,13] The systems we are interested in include glasses and imperfect crystals as special cases. However, to be specific, we will only consider glasses below; the discussion is valid for all non-equilibrium systems.

We hope that the proofs of the above two theorems settle the controversy between the two forms of glasses and about the residual entropy S_R.

We first consider the behavior of the thermodynamic entropy that appears in classical non-equilibrium thermodynamics. As is well known, this entropy is governed by the second law.[42] In the next section, we prove Theorem 1. In the following section, we prove Theorem 2. Both sections deal with the thermodynamic entropy. In Sect. IV, we explain how the thermodynamic residual entropy can be understood in terms probability of a microstate, and how even a single sample can give a highly reliable result for the residual entropy. The last section contains our conclusions.

II.   FORWARD ENTROPY BOUND DURING VITRIFICATION: THEOREM 1

The process we consider is carried out at some cooling rate as follows. The temperature of the medium is isobarically changed by some small but fixed ΔT_0 from the current value to the new value, and we wait for (not necessarily fixed) time τ_{obs} at the new temperature to make an instantaneous measurement on the system before changing the temperature again. At some temperature $T_{0\text{g}}$, see Fig. 1, the relaxation time τ_{relax}, which continuously increases as the temperature is lowered, becomes equal to τ_{obs}. Just below $T_{0\text{g}}$, the structures are not yet frozen; they "freeze" at a lower temperature $T_{0\text{G}}$ (not too far from $T_{0\text{g}}$) to form an amorphous solid with a viscosity close to 10^{13} poise. This solid is identified as a *glass*. The location of both temperatures depends on the rate of cooling, i.e. on τ_{obs}. Over the glass transition region between $T_{0\text{G}}$ and $T_{0\text{g}}$ shown in Fig. 1, the *non-equilibrium* liquid gradually turns from an equilibrium supercooled liquid at or above $T_{0\text{g}}$ into a glass at or below $T_{0\text{G}}$, a picture already known since Tammann.[34] Over this region, some dynamical properties such as the viscosity vary continuously but very rapidly. However, thermodynamic quantities such as the volume or the enthalpy change continuously but slowly. As the observation time τ_{obs} is increased, the equilibrated supercooled liquid continues to lower temperatures before the appearance of $T_{0\text{g}}$. In the *hypothetical limit* $\tau_{\text{obs}} \to \infty$, it is believed that the equilibrated supercooled liquid will continue to lower temperatures without any interruption, and is shown schematically by the solid blue curve in Fig. 1. We overlook the possibility of the supercooled liquid ending in a spinodal.[44] It is commonly believed that this entropy will vanish at absolute zero ($S_{\text{SCL}}(0) \equiv 0$), as shown in the figure. As we are going to be interested in $S_{\text{SCL}}(T_0)$ over $(0, T_{0\text{g}})$, we must also acknowledge the possibility of an ideal glass transition in the system. If one believes in an ideal glass transition, then there would be a

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singularity in $S_{\mathrm{SCL}}(T_0)$ at some positive temperature $T_{\mathrm{K}} < T_{0\mathrm{G}}$, below which the system will turn into an ideal glass whose entropy will also vanish at absolute zero.[34] The possibility of an ideal glass transition, which has been discussed in a recent review elsewhere,[38] will not be discussed further in this work. All that will be relevant in our discussion here is the fact that the entropy vanishes in both situations ($S_{\mathrm{SCL}}(0) \equiv 0$). However, it should be emphasized that the actual value of $S_{\mathrm{SCL}}(0)$ has no relevance for the theorems.

It is a common practice to think of the glass transition to occur at a point that lies between $T_{0\mathrm{g}}$ and $T_{0\mathrm{G}}$. Gupta and Mauro[32] consider the glass transition to occur at $T_{0\mathrm{G}}$ to obtain the bound in Eq. (1). We will not make this assumption in this work except when we discuss their inequality later. We have drawn the two entropy curves (Glass1 or Glass2) in Fig. 1 that emerge out of $S_{\mathrm{SCL}}(T_0)$ for a given τ_{obs} in such a way that Glass1 has its entropy above (so that $S_{\mathrm{R}} \geq 0$) and Glass2 below (so that $S_{\mathrm{R}} \equiv 0$) that of the supercooled liquid. The entropy of Glass1 (Glass2) approaches that of the equilibrated supercooled liquid entropy from above (below) during isothermal (fixed temperature of the medium) relaxation; see the two downward vertical arrows for Glass1. It is the approach to equilibrium that distinguishes the two glasses, Glass1 and Glass2. Although Johari and Khouri do not mention in their conclusion, their analysis of tight bounds also shows that the entropy *does not* drop by an amount close to S_{R} within the glass transition region for the systems studied by them. However, because of the involved approximation, it sheds no light on whether the glass entropy lies above or below the corresponding $S_{\mathrm{SCL}}(T_0)$. Thus, their work and many others leave open the possibility that Glass2 may materialize if the irreversibility is too large. This again shows why obtaining a bound is so important, even if we do not determine the actual entropy values.

The concept of internal equilibrium[43,45] for a non-equilibrium system means that its instantaneous entropy is a state function of its instantaneous state variables like energy, volume etc. and any internal variables[43,45–48] used to specify its state. Their usage is also a common practice[34,35] now-a-days for glasses. Employing internal equilibrium gives rise to an instantaneous Gibbs fundamental relation, see Eq. (14) below, which determines its instantaneous temperature, pressure, etc.

We now prove Theorem 1. Consider an isobaric process (we will not explicitly exhibit the pressure in this section) from some state A at temperature T_0 in the supercooled liquid state which is still higher than $T_{0\mathrm{g}}$ to the state A_0 at absolute zero. The state A_0 depends

on the path A→A$_0$ along with $T_0 = 0$, which is implicit in the following. We have along A→A$_0$

$$S(0) = S(T_0) + \int_A^{A_0} d_e S + \int_A^{A_0} d_i S, \tag{6}$$

where we have assumed that there is no latent heat in the vitrification process, and where[43,45–48] $dS = d_e S + d_i S$, each of which for a non-equilibrium system is path dependent. The component

$$d_e S(t) = -dQ(t)/T_0 \equiv C_P dT_0/T_0 \tag{7}$$

represents the reversible entropy exchange with the medium in terms of the heat $dQ(t)$ given out by the glass at time t to the medium whose temperature at that instant is T_0. The component $d_i S > 0$ represents the irreversible entropy generation in the irreversible process. In general, the *irreversible* term

$$d_i S \geq 0 \tag{8}$$

contains, in addition to the contribution from the irreversible heat transfer with the medium, contributions from all sorts of viscous dissipation going on *within* the system and normally require the use of internal variables.[43,45–48] Thus, Eq. (6) contains *all* possible sources of entropy variations.[43,45–48] This is easily proven by considering the system and the medium as an *isolated system*[43,45] and expressing the entropies as functions of the instantaneous values of the *observables* and *internal variables*. A discontinuous change in the entropy is ruled out from the continuity of the Gibbs free energy G and the enthalpy H in vitrification proved elsewhere.[43] Thus, we only consider a continuous change in the entropy as shown by the two glass curves in Fig. 1.

The equality in Eq. (8) holds for a reversible process, which we will no longer consider unless stated otherwise. The strict inequality $d_i S > 0$ occurs only for irreversible process such as in a glass. Since the second integral in Eq. (6) is always *positive*, and since the residual entropy S_R is, by definition, the entropy $S(0)$ at absolute zero, we obtain the important result

$$S_R \equiv S(0) > S_{\text{expt}}(0) \equiv S(T_0) + \int_{T_0}^0 C_P dT_0/T_0. \tag{9}$$

This confirms the expectation noted above that the irreversibility during vitrification does not allow for the determination of the entropy exactly, because determining the second integral in Eq. (6) is not trivial, especially if internal variables are not considered.[34,45] The forward inequality is due to the irreversible entropy generation from all possible sources[43,45–48]

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that seems to not have been recognized by the proponents[7,8,10,32,33] of vanishing S_R. This strict forward inequality clearly establishes that the residual entropy at absolute zero must be strictly larger than $S_{\text{expt}}(0)$ in any non-equilibrium process. This proves the first inequality in Eq. (4).

We now prove the second inequality in Eq. (4). We consider processes that occur when $\tau_{\text{obs}} < \tau_{\text{relax}}(T_0)$. Let $\dot{Q}(t) \equiv dQ(t)/dt$ be the rate of net heat loss by the system. Then, for each temperature interval $dT_0 < 0$ below T_{0g}, we have

$$|dQ| \equiv C_P \, |dT_0| = \int_0^{\tau_{\text{obs}}} \left| \dot{Q} \right| dt < |dQ|_{\text{eq}} (T_0) \equiv \int_0^{\tau_{\text{relax}}(T_0)} \left| \dot{Q} \right| dt, \quad T_0 < T_{0g}$$

where $|dQ|_{\text{eq}} (T_0) > 0$ denotes the net heat loss by the system to come to equilibrium, i.e. become supercooled liquid during cooling at T_0. For $T_0 \geq T_{0g}$, we have $dQ \equiv dQ_{\text{eq}}(T_0)$. Thus,

$$\int_{T_0}^0 C_P dT_0/T_0 > \int_{T_0}^0 C_{P,\text{eq}} dT_0/T_0,$$

where $|dQ|_{\text{eq}} \equiv C_{P,\text{eq}} \, |dT_0|$. We thus conclude that

$$S_{\text{expt}}(0) > S_{\text{SCL}}(0); \tag{10}$$

the strict inequality is the result of the fact that glass is a non-equilibrium state. Otherwise, we will have $S_{\text{expt}}(0) \geq S_{\text{SCL}}(0)$ for any arbitary state.

This proves Theorem 1.

The difference $S_R - S_{\text{expt}}(0)$ would be larger, more irreversible the process is. The quantity $S_{\text{expt}}(0)$ can be determined calorimetrically by performing a cooling experiment. We take T_0 to be the melting temperature T_{0M}, and uniquely determine the entropy of the supercooled liquid at T_{0M} by adding the entropy of melting to the crystal entropy $S_{\text{CR}}(T_{0M})$ at T_{0M}. The latter is obtained in a unique manner by integration along a reversible path from $T_0 = 0$ to $T_0 = T_{0M}$:

$$S_{\text{CR}}(T_{0M}) = S_{\text{CR}}(0) + \int_0^{T_{0M}} C_{P,\text{CR}} dT_0/T_0,$$

here, $S_{\text{CR}}(0)$ is the entropy of the crystal at absolute zero, which is traditionally taken to be zero in accordance with the third law, and $C_{P,\text{CR}}(T_0)$ is the isobaric heat capacity of the crystal. This then uniquely determines the entropy of the liquid to be used in the right hand side in Eq. (9). We will assume that $S_{\text{CR}}(0) = 0$. Thus, the experimental determination of $S_{\text{expt}}(0)$ is required to give the *lower bound* to the residual entropy in Eq.

(4). Experiment evidence for a non-zero value of $S_{\text{expt}}(0)$ is abundant as discussed by several authors;[3,9,12,13,20,21] various textbooks[34,35] also discuss this issue. Goldstein[9] gives a value of $S_{\text{R}} \simeq 15.1$ J/K mol for o-terphenyl from the value of its entropy at $T_0 = 2$ K. However, we have given a mathematical justification of $S_{\text{expt}}(0) > 0$ in Eq. (10). The strict inequality proves immediately that the residual entropy *cannot* vanish for glasses, which justifies the curve Glass1 in Fig. 1.

The inequality in Eq. (9) takes into account any amount of irreversibility during vitrification; it is no longer limited to only small contributions of the order of 2% considered by Johari and Khouri and by several others,[9,14,34,35] which makes our derivation very general. The relevance of the residual entropy has been discussed by several authors in the literature.[9,12–15,17–19,30]

By considering the state A_0 above to be a state A_0 of the glass in a medium at some arbitrary temperature T_0' below T_{0g}, we can get a generalization of Eq. (9):

$$S(T_0') > S_{\text{expt}}(T_0') \equiv S(T_0) + \int_{T_0}^{T_0'} C_P dT_0/T_0. \tag{11}$$

We again wish to remind the reader that all quantities depend on the path $A \rightarrow A_0$, which we have not exhibited. By replacing T_0 by the melting temperature T_{0M} and T_0' by T_0, and adding the entropy $\widetilde{S}(T_{0M})$ of the medium on both sides in the above inequality, and rearranging terms, we obtain (with $S_{\text{L}}(T_{0M}) = S_{\text{SCL}}(T_{0M})$ for the liquid)

$$S_{\text{L}}(T_{0M}) + \widetilde{S}(T_{0M}) \leq S(T_0) + \widetilde{S}(T_{0M}) - \int_{T_{0M}}^{T_0} C_P dT_0/T_0, \tag{12}$$

where we have also included the equality for a reversible process. This provides us with an independent derivation of the inequality given by Setna and coworkers.[31]

It is also clear from the derivation of Eq. (10) that the inequality can be generalized to any temperature $T_0 < T_{0g}$ with the result

$$S_{\text{expt}}(T_0) > S_{\text{SCL}}(T_0), \tag{13}$$

with $S_{\text{expt}}(T_0) \rightarrow S_{\text{SCL}}(T_0)$ as $T_0 \rightarrow T_{0g}$ from below. Thus, $S_{\text{expt}}(T_0)$ appears in form similar to that of Glass3 in Fig. 1, except that the latter represents a possible glass entropy while the former represents the calorimetric approximation for Glass1.

While we have only demonstrated the forward inequality, the excess $S_{\text{R}} - S_{\text{expt}}(0)$ can be computed in non-equilibrium thermodynamics,[43,45–48] which provides a clear prescription

for calculating the irreversible entropy generation. We do not do this here as we are only interested in general results, while the calculation of irreversible entropy generation will, of course, be system-dependent and will require detailed information. Gutzow and Scmelzer[12] provide such a procedure with a single internal variable but under the assumption of equal temperature and pressure for the glass and the medium. However, while they comment that $d_\mathrm{i}S \geq 0$ whose evaluation requires system-dependent properties, their main interest is to only show that it is negligible compared to $d_\mathrm{e}S$.

We have proved Theorem 1 by considering only the system without paying any attention to the medium but assuming the second law as is evident from Eq. (8). We have done this because the proponents of vanishing S_R normally consider the glassy state without ever bringing in the medium in the discussion. This does not mean that the conclusion would be any different had we brought the medium into our discussion. This is seen from the derivation of the ineqaulity in Eq. (12) from Eq. (11). We will find it convenient to consider the medium in the next section to overcome the objection[8,10] that the glass does not obey the second law.

III.   ENTROPY AND ENTHALPY DURING RELAXATION

We now turn to the inequality in Eq. (1) to see if it would ever be satisfied. To avoid directly discussing the relationship of the latent heat with the entropy loss, the possibility of entropy loss, or whether the second law applies to a glass, we change our mode of presentation and consider the system not by itself, but as a part of an isolated system in which the system is surrounded by an *extremely large* medium whose temperature T_0, pressure P_0, etc. are not affected by what happens within the system. To prove Theorem 2, we consider the system to be not in equilibrium with the medium. All processes that go on within the medium occur at constant temperature, pressure, etc. Thus, there will not be any irreversible process going on within the medium. All irreversible processes will go on within the system. This simplification occurs because of the extremely large size of the medium and will be central in our discussion here.

While some may doubt that the second law is not applicable to the glass at the glass transition, there cannot be any doubt that the second law applies to the isolated system. It is found[43,45,49] that the instantaneous temperature $T(t)$, pressure $P(t)$, etc. of the system are

different from the corresponding quantities of the medium when the former is not in equilibrium with the medium. All that is required is for the system to be in *internal equilibrium*,[43,45] which is defined as a state in which the entropy has no explicit time-dependence; its time variation is due to time-dependent observables and internal variables. The existence of instantaneous $T(t)$, $P(t)$, etc. is a consequence of internal equilibrium, and is a general property of any system out of equilibrium even at high temperatures and is not restricted to glasses only. Therefore, $T(t)$, $P(t)$, etc. should not be confused with fictive temperature and pressure, etc. that are meaningful for glasses. This issue has been discussed earlier.[43] The Gibbs fundamental relation for the system when it is in internal equilibrium is given by

$$dE(t) = T(t)dS(t) - P(t)dV(t) - A(t)d\xi(t), \tag{14}$$

where we have allowed for a single internal or structure variable $\xi(t)$ for the sake of simplicity; for glasses, see Nemilov[34] and Gutzow and Schmelzer[35] for the usage of internal variables. We have explicitly shown the time-dependence in the above equation to highlight the presence of relaxation in the system. The affinity $A(t)$ is conjugate to the internal variable and vanishes when the system comes to equilibrium with the medium ($A_0 \equiv 0$). In that case, we also have $T(t) \to T_0$ and $P(t) \to P_0$; see Eq. (15).

For a system out of equilibrium, the instantaneous entropy $S(t)$ and volume $V(t)$ seem to play the role[43] of "internal variables," whose "affinities" are given by $T(t) - T_0$ and $P(t) - P_0$, respectively. This fact is not common in the glass literature to the best of our knowledge. The temperature and pressure of the system are usually taken to be those of the medium, which is an approximation. For example, Schmelzer and Gutzow[50] identify $d_e S = C_P dT/T$, see their Eq. (1), whereas it should be properly identified as in Eq. (7) with T replaced by T_0. They also identify the pressure in their Gibbs fundamental relation [see their Eq. (2)] as the external pressure.

We now turn to prove Theorem 2. Let us rewrite the Gibbs fundamental relation as

$$dE(t) = T_0 dS(t) - P_0 dV(t) + (T(t) - T_0)dS(t) - (P(t) - P_0)dV(t) - A(t)d\xi(t), \tag{15}$$

in which each of the last three terms can be associated with an irreversible entropy generation.[43] For this, it is easier to take all but the first term on the right side to the other side of the equation. We thus note[43] that

$$(T_0 - T(t))dS(t) \geq 0, (P(t) - P_0)dV(t) \geq 0, A(t)d\xi(t) \geq 0, \tag{16}$$

in accordance with the second law. The equalities above and below occur only for reversible processes. As we are only interested in irreversible processes in non-equilibrium systems, the inequalities above and below become strict inequalities, which cannot be violated in any real process. Thus, as before, we will exploit these *strict* inequalities to derive a bound on the rate of entropy variation.

We extend the derivation given earlier[43] to include the internal variable to obtain as the statement of the second law:[42]

$$\frac{dS_0(t)}{dt} = \left(\frac{1}{T(t)} - \frac{1}{T_0}\right)\frac{dE(t)}{dt} + \left(\frac{P(t)}{T(t)} - \frac{P_0}{T_0}\right)\frac{dV(t)}{dt} + \frac{A(t)}{T(t)}\frac{d\xi(t)}{dt} \geq 0; \qquad (17)$$

each term in the first equation must be non-negative. In a vitrification process, in which the energy decreases with time, we must, therefore, have

$$T(t) \geq T_0$$

during any relaxation (at a fixed temperature and pressure of the medium) so that $T(t)$ approaches T_0 from above $[T(t) \to T_0^+]$ as the relaxation ceases and the equilibrium is achieved. It now follows from Eq. (16) that during vitrification

$$dS(t)/dt \leq 0; \qquad (18)$$

the equality occurring only when equilibrium with the medium has been achieved. The above inequality gives the bound on the rate that we are interested in. At the end of the relaxation

$$S(T_0, P_0, t) \stackrel{t \to \infty}{\Rightarrow} S_{\mathrm{SCL}}^+(T_0, P_0);$$

the plus sign is to indicate that the glass entropy reaches $S_{\mathrm{SCL}}(T_0, P_0)$ from above.

We have shown T_0, P_0 in $S(T_0, P_0, t) \equiv S(T(t), P(t), A(t))$ to emphasize that the result is general during any relaxation. In the derivation, which only considers the behavior of $S_0(t)$ of the isolated system, no assumption about the nature of irreversibility such as any loss of ergodicity in the system, inapplicability of the second law to the system, possibility of any chaotic behavior, chemical reaction, etc. is made. The only assumption that has been made is that it is possible to define the instantaneous temperature and pressure for the system. We have also made no assumption that $S(t)$ lies above (Glass1, Glass3) or below (Glass2) the entropy $S_{\mathrm{SCL}}(T_0)$ of the equilibrated supercooled liquid; see Fig. 1. Being a general result, it should be valid for any real glass. This now gives a way to decide which

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of the glasses in Fig. 1 is in accordance with the above conclusion. Above T_{0g}, the system is always in equilibrium with the medium so its temperature is the same as T_0. Below T_{0g}, when the system is not in equilibrium with the medium, then $T(t) > T_0$ as long as there is no equilibrium. The entropy of Glass1 and Glass3 approach $S_{SCL}(T_0)$ of the equilibrated supercooled liquid from above during any isothermal relaxation, which is consistent with Eq. (18). As the entropy is a unique function of the path, the two glasses must correspond to different histories. Therefore, from now on, we will not consider Glass3 anymore.

For Glass2 in Fig. 1, the entropy actually drops below that of the supercooled liquid by some amount;[3-8,32,33] the amount does not even have to be comparable to S_R. In this situation, the entropy must approach $S_{SCL}(T_0)$ of the supercooled liquid from below during relaxation; see the upward arrow in Fig. 1. This will result in the increase of the entropy during relaxation, which violates Eq. (18). Thus, Glass2 cannot be rationalized. For the same reason, the conclusion of Gutzow and Schmelzer[12] of increase in entropy cannot be rationalized.

We are now ready to investigate what could be technically wrong with the entropy loss proposal. This will also settle whether the glass must obey the second law or not at the glass transition. From the behavior of $dS_0(t)/dt$ in Eq. (17), we can immediately identify[43,45] the rates for the entropy of the system and the medium, respectively,

$$\frac{dS(t)}{dt} = \frac{1}{T(t)}\frac{dE(t)}{dt} + \frac{P(t)}{T(t)}\frac{dV(t)}{dt} + \frac{A(t)}{T(t)}\frac{d\xi(t)}{dt}.$$

$$\frac{d\widetilde{S}(t)}{dt} = -\frac{1}{T_0}\frac{dE(t)}{dt} - \frac{P_0}{T_0}\frac{dV(t)}{dt}.$$

While the entropy change of the medium has no irreversible contribution as noted earlier, the irreversible entropy change $d_iS(t)$ of the system is given by the three terms in Eq. (17), each of which must be non-negative. Writing $dS(t) = d_eS(t) + d_iS(t)$, we find that

$$\frac{d_eS(t)}{dt} = -\frac{d\widetilde{S}(t)}{dt} = \frac{1}{T_0}\frac{dE(t)}{dt} + \frac{P_0}{T_0}\frac{dV(t)}{dt}$$

$$\frac{d_iS(t)}{dt} = \frac{dS_0(t)}{dt} \geq 0.$$

In general, $d_eS(t)/dt$ can have either sign. In a cooling process, we have $dE(t)/dt < 0$. Moreover, we normally have $dV(t)/dt < 0$. Thus, $d_eS(t)/dt < 0$. However, its sign is not relevant for our discussion. On the other hand, $d_iS(t)/dt \geq 0$, which follows from the second law applied to the isolated system, for which there is no dispute. With these consequences

of the second law, we can now evaluate the merit of the entropy loss proposal.[7,8,10,32,33] Let us consider vitrification. The change in the entropy $d_e S(t) < 0$ is due to exchanges with the medium. This is part of the entropy change that will occur even in a reversible process. The contribution from the entropy loss,[7,8,10,32,33] which we denote by $dS_{loss}(t)$, is due to the vitrification process. Vitrification in the entropy loss view represents changes occurring *within* the system. As the contribution from every internal process must be included in $d_i S(t)$, and as each such contribution must be *non-negative*, there is no way to justify the negative contribution $dS_{loss}(t)$ due to vitrification[7,8,10,32,33] without violating the second law for the isolated system. This proves Theorem 2.

This is the conclusion obtained by Goldstein;[9] we have just provided a direct proof of his conclusion. There is also no merit to the suggestion of Gupta and Mauro[8,10,32] that the glass does not obey the second law.

It is easy to see that the discussion above can be easily extended to include other observables and internal variables without affecting Theorem 2. The above discussion was also not restricted to a constant pressure of the medium. Indeed, the discussion above has been very general. The only restriction was the extremely large size of the medium, which is easily satisfied in experiments. For the general case, the Gibbs free energy is given by $G(t) = H(t) - T_0 S(t)$. At fixed T_0, we have[43]

$$\frac{dG(t)}{dt} = \frac{dH(t)}{dt} - T_0 \frac{dS(t)}{dt} \leq 0, \tag{19}$$

from which it follows that

$$\left| \frac{dH(t)}{dt} \right| \geq T_0 \left| \frac{dS(t)}{dt} \right|.$$

We now turn to considering isobaric vitrification during which the system is not in equilibrium with the medium. We will assume that the system is always very close to mechanical equilibrium so that its pressure is equal to P_0; however, there is normally no thermal equilibrium so that the instantaneous temperature $T(t)$ of the system is different from T_0. We will now show that the above general conclusion remains unaltered. From Eq. (14), we have

$$\left| \frac{dH(t)}{dt} \right| \geq T(t) \left| \frac{dS(t)}{dt} \right|, \tag{20}$$

where we have used $A(t) d\xi(t)/dt \geq 0$. The last bound is tighter than the previous bound and reduces to the equality obtained earlier[43] in the absence of any internal variable ξ. In any case, the enthalpy of the glass is not constant in time at T_{0G} even for an isobaric

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vitrification if we accept that the entropy undergoes relaxation. We thus conclude that there is no justification in assuming $\Delta H(T_{0G}) = 0$.

We now turn to the inequality in Eq. (1) to inquire what may be wrong with its trivial justification offered by its authors. We consider $T_0 \leq T_{0G}$. The enthalpy $H(T_0)$ of the glass relaxes towards its equilibrium value $H_{SCL}(T_0)$ of the supercooled liquid from above during isobaric vitrification, contrary to the assumption by Gupta and Mauro.[2] Acknowledging this immediately leads to

$$T_{0G}(S(T_{0G}) - S_{SCL}(T_{0G})) \leq H(T_{0G}) - H_{SCL}(T_{0G}).$$

As the right side is strictly positive, there is no justification in concluding the inequality in Eq. (1). It is most certainly possible to satisfy the above inequality and also have

$$S(T_{0G}) \geq S_{SCL}(T_{0G}).$$

This is consistent with strict inequality in Eq. (18). The equality $\Delta H(T_0) = 0$ is only valid at T_{0g}, where the difference $\Delta S(T_0) = 0$, so that $S(T_{0g}) = S_{SCL}(T_{0g})$.

The isothermal relaxation that occurs during glassy vitrification originates from the tendency of the glass to come to thermal equilibrium during which its temperature $T(t)$ approaches T_0 in time. The relaxation process results in the lowering of the corresponding Gibbs free energy[43] in time, as expected; this results in not only lowering the enthalpy during vitrification, as observed experimentally, but also of the entropy $S(t)$ during relaxation, as shown for Glass1 in Fig. 1.

IV. STATISTICAL INTERPRETATION OF THERMODYNAMIC S_R

Now that we have established the reality of the residual entropy S_R by considering the thermodynamic entropy in classical thermodynamics, we wish to discuss its possible statistical interpretation. We recall that the thermodynamic entropy cannot be given a unique value; all that we can discuss in thermodynamics is the change in it. It does not even have to be non-negative, as is evident from the entropy of an ideal gas at very low temperature. However, as we have defined $S(T_0, t)$ with respect to $S_{CR}(0)$ in this work, and we have taken $S_{CR}(0) = 0$, the thermodynamic entropy has a *unique* value. Therefore, any attempt to provide a statistical interpretation must result in an agreement with the numerical value

of the above thermodynamic entropy, a point also made by Sethna and coworkers.[31] The issue of the statistical interpretation has been discussed elsewhere by us.[14,15] As a glass is a frozen structure (over an extremely long period of time), we index each frozen structure, which represents a microstate, at absolute zero by $i = 1, 2, \cdots, W_G$. Each microstate is characterized by the set of observables and internal variables. All glasses formed under *identical macroscopic conditions* will be in one of these microstates at $T_0 = 0$; let $p_i > 0$ denote the probability that a glass will be in the microstate i. The instantaneous statistical entropy is an average quantity[15,16] (we set $k_B = 1$): $S(t) = -\langle \ln p \rangle \equiv \sum_i p_i(-\ln p_i)$. If the glass formation occurs under an unbiased condition, all microstates will be equally probable ($p_i \equiv p = 1/W_G$ for all i) so that the residual entropy is $S_R = \ln W_G$. The necessary (but not sufficient) condition for this is that the system be macroscopically large. The sufficient condition requires the system to be in internal equilibrium, though not necessarily in equilibrium with the medium, as discussed elsewhere.[43] In this case, the contribution $-\ln p = \ln W_G$ to the entropy from any of the W_G microstates is the same so that

$$S = -\ln p = \ln W_G; \tag{21}$$

there is no need to sum over all microstates since $\sum_i p_i = 1$. Just one microstate will give us the correct entropy. Similarly, just one microstate will give a highly reliable value of any thermodynamic quantity. As the equiprobable condition will be overwhelmingly satisfied for a system in internal equilibrium, just one glass sample will give us a highly reliable thermodynamics. The discussion can be applied to a system at any temperature, provided it is in internal equilibrium. There is no need to carry out an ensemble or time average. This is what makes classical thermodynamics such a robust and highly reproducible endeavor, a result quite well known in equilibrium. We have just extended it to systems in internal equilibrium.

Just because a glass sample at absolute zero is in a single microstate does not mean that its statistical entropy is zero. Such a statistical entropy interpretation does not agree with the thermodynamic entropy which, as discussed above, is known to yield a non-zero residual entropy in many cases. Therefore, such an interpretation, the one taken by Kivelson and Reiss[7] and by Gupta and Mauro,[8] must be considered physically irrelevant. The correct statistical formulation of the entropy is given by $-\ln p$, as shown in Eq. (21), and merely reflects the sample *probability* of a glass prepared under identical macroscopic

conditions.[14] Any sample will give the same statistical entropy equal to the thermodynamic residual entropy so that the statistical and thermodynamic interpretations of the entropy are equivalent.

The discussion should not imply that the ensemble average is no longer meaningful just because we are dealing with a single sample. The way to see it most clearly is to imagine dividing the system into a macroscopically large number of quasi-independent subsystems, each of which itself is macroscopically large. The subsystems are identical in size. Let ι denote a microstate of one of these subsystems, and $p_\iota > 0$ its probability. Then, it follows from their quasi-independence that $p = \prod_k p_\iota$; the product is over all subsystems. It is now easy to see that

$$S = \sum S_k,$$

where the sum is over all subsystems; each subsystem can be considered as representing a member of the ensemble. All these members are considered at the same instant.

Recently, Goldstein[40] has also discussed the relevance of a single microstate for the average at any temperature, but he does not discuss the time required for the system to come to internal equilibrium or to equilibrium after adding the enthalpy increment to it. Thus, it is by no means clear that a single microstate during this time will really represent the average properties of the system. His requirement of "...overwhelming majority of microstates..." must refer to the equilibrium state of minimum Gibbs free energy at given T_0, P_0, but this is not relevant for a glass. As the enthalpy increment is added, it takes a while for this enthalpy to distribute itself throughout the system from the boundary. During this interval, the system becomes *inhomogeneous* and will not even be in internal equilibrium, let alone in equilibrium. In this interval, we can still treat each subsystem discussed above in internal equilibrium. But then we are dealing with an ensemble average over inhomogeneous subsystems. We believe that his conclusion would be valid only after the system has come into internal equilibrium, though not necessarily in equilibrium, as demonstrated above. For this, we must replace his above requirement by equiprobability of microstates.

V.   CONCLUSIONS

The current work was motivated by the confusion about the residual entropy and about the behavior of the entropy during relaxation that exists in the literature, as discussed in

Sect. I A. There are opposing views not only about the residual entropy but also about the impact of Goldstein's observation for the latter. The use of calorimetric data so far has been to demonstrate that the irreversibility during a glass transition is minimal so that $S_{\mathrm{expt}}(T_0)$ is not different from the actual thermodynamic entropy $S(T_0)$ of the glass. But the calorimetric evidence does not reveal how $S(T_0)$ or $S_{\mathrm{expt}}(T_0)$ relate to $S_{\mathrm{SCL}}(T_0)$. Therefore, how $S(T_0)$ approaches $S_{\mathrm{SCL}}(T_0)$ remains unsettled; there are competing views in the literature. To clarify the situation, we have considered the role of irreversible entropy generation during isobaric vitrification and prove Theorems 1 and 2 that are valid regardless of how far the system is out of equilibrium, as long as it is in internal equilibrium; the latter is required to define the instantaneous temperature, pressure, affinity, etc. The theorems are very general and are not restricted by the "amount" of irreversibility. Theorem 1 shows that the calorimetrically measured absolute zero entropy forms a *strict* lower bound to the residual entropy. The former is shown to be positive under the assumption $S_{\mathrm{SCL}}(0) = 0$; otherwise, we have the strict inequality in Eq. (10) for a glass. In general, we have $S_{\mathrm{expt}}(0) \geq S_{\mathrm{SCL}}(0)$. It then follows that the residual entropy has to be larger than $S_{\mathrm{expt}}(0)$. Theorem 2 shows that the instantaneous entropy $S(T_0, t)$ must always be higher than or at most equal to the entropy $S_{\mathrm{SCL}}(T_0)$ of the equilibrated supercooled entropy, which invalidates the inequality in Eq. (1). During isothermal relaxation, the entropy must decrease towards $S_{\mathrm{SCL}}(T_0)$ in time. All physical systems must follow the two inequalities in Eqs. (4-5) without any *exception.* We have demonstrated that the entropy loss proposal violates the second law and have put the original observation of Goldstein on firmer grounds. We have not only justified but also strengthened the calorimetric evidence of the residual entropy by establishing $S_{\mathrm{R}} > S_{\mathrm{expt}}(0) > S_{\mathrm{SCL}}(0)$.

The theorems follow from considering the thermodynamic entropy that appears in the second law for an isolated system. Thus, any attempt to provide a statistical version of entropy must satisfy these two consequences. We have shown that the conventional statistical entropy formulation is consistent with the thermodynamic notion of the residual entropy and that the equiprobability requirement explains why a single sample is sufficient to give a highly reliable thermodynamics of the system even when the latter is not be in equilibrium with the medium.

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* Electronic address: pdg@uakron.edu

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